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An investigation of the factors influencing the design of a dense prilled ammonium nitrate-fuel oil mixture

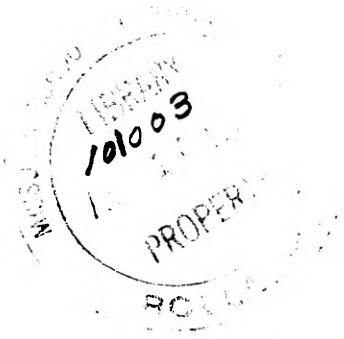
Robert Bartley Hopler Jr.

Department:

AN INVESTIGATION OF THE FACTORS INFLUENCING THE DESIGN OF A DENSE PRILLED AMMONIUM NITRATE-FUEL OIL MIXTURE

BY

ROBERT BARTLEY HOPLER, JR



A

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Approved by

George B. Leland (advisor)

Wm J. James

Carl R. Nuelsen

Paul Dean Proctor

ABSTRACT

The physical characteristics of dense ammonium nitrate prills were examined. The density was found to be 1.52 grams per cubic centimeter, and from this the specific surface was calculated for the size fractions of interest in the investigation. Theoretical loading densities were calculated for between 26.0 and 47.6 percent voids.

The explosive properties of discrete particle size fractions were investigated. The equation by Clark was found to predict the detonation velocity of the sizes smaller than 8/20 mesh. The equation by Cook could not be applied to dense prilled ammonium nitrate. The possibility of a very oxygen negative condition existing with the largest prills was investigated.

Tests showed that dense prilled ammonium nitrate-fuel oil mixtures became more sensitive as their particle size decreased. The number of prills contacting the primer was found to be approximately a constant for the particle size ranges investigated. This was attributed to the effect of "hot-spots" on initiation of detonation.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. George B. Clark, Chairman of the Department of Mining Engineering at the Missouri School of Mines and Metallurgy, for his guidance and assistance throughout the course of this work.

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CHAPTER I

INTRODUCTION

Ammonium nitrate has long been used as a component of explosives. In World War I it reached its first major utilization other than in the ammonia dynamites, when it was brought into the war effort as the major component of "amatol" (Field, 1947). In the mid 1930's the first ammonium nitrate-fuel came into use as packaged Du Pont "Nitramon" (Maxon, 1935). Since the Second World War events occurred which changed the explosives industry, and ammonium nitrate has become the most used explosive substance in the United States.

One major cause of the ammonium nitrate (generally abbreviated AN) revolution in blasting was the Second World War itself. Near the midpoint of the war there arose a critical shortage of fixed nitrogen all over the world caused by the use of nitrogen compounds in explosives. As the demand diminished near the end of the war, American nitrogen plants were coming into production. The demand that then arose for fertilizer nitrogen, particularly in Europe, became so great that munitions-grade AN was made available to the fertilizer industry (Sauchelli, 1960). In the fiscal year ending June 30, 1948, U.S. Army ordnance plants shipped 779,730 tons of AN fertilizer to Germany, Japan, and Korea (Burns, et al, 1953).

The explosibility of AN had long been known, and was further brought to light in the disasters at Texas City, Texas; Brest, France; and the Black Sea. In fact, in the 40 years previous to 1955, there had been more than 25 major fires and explosions, involving 12,000 tons of AN and resulting in death or injury to some 5,000 persons (Hainer, 1955). Thus, many groups began to look for a way to use this low-cost explosive energy

to a greater extent in the commercial field.

In approximately 1947, this material became more economical to produce by the advent of the prilling process which was then adapted to its manufacture. Even then, however, obstacles remained in the way of its use as a blasting agent. One of the major problems remaining was the fact that AN is extremely soluble in water, and up to that time most quarry drilling was done by the wet process of churn drilling. In this process, several feet of water are usually left in the bottom of a hole due to the usual design of the bailing device. The use of suitable dry rotary drills, introduced in the post-war years, therefore was another of the factors which entered into the major change in blasting which was to take place (Ammons, 1959).

The first major use of AN as an explosive that was to be mixed at the blast property was by Lee and Akre in 1954 at the Maumee Collieries Co. in Indiana (Cooley, 1955). Since in the molecule of AN there is an extra atom of oxygen over that necessary to produce the reaction products N_2 and H_2O some form of carbon must be added to achieve optimum results. In the case mentioned, carbon black was used. The mixture was then sealed in a polyethylene bag. The reports of this commercial use created great excitement in the industry, but the mix still had some undesirable qualities. These were primarily the low density of the large porous particles, and the difficulty in initiation of the mixture.

It was soon discovered, however, that the porous nature of the regular AN prill could be used to advantage. When a hydrocarbon in the liquid form, such as diesel fuel, was poured over the AN, a mixture resulted which was the proper combination to utilize the excess oxygen. This gave a free flowing, easily detonated blasting agent.

Research was continued by users, manufacturers, and other interested scientific groups in an effort to solve the problems of low density and poor water resistance in a field mix, and also to increase the range of sensitivity and detonation velocity of the prill and oil mixture. During the intervening time the use of the AN-fuel mixes was growing at a fantastic rate, since the desirable qualities inherent in the mix far outweighed those that were undesirable.

A new prilled product, non-porous in nature and smaller in size than the regular AN prill, has recently been introduced to the fertilizer industry. The lack of pores, while increasing the density, adversely effects the intimacy of contact between the AN and fuel when used as a blasting agent. The present investigation was carried out in order to determine the explosive properties of various particle sizes of this new product.

A. SCOPE OF THE INVESTIGATION

1. Statement of the problem. While much is known of the detonation properties of regular prilled fertilizer grade AN, comparatively little is known of the characteristics of the dense prilled variety. This material, being of radically different physical character from regular porous prills, offers a new horizon in the AN-fuel field. The differences in character include greater sphericity, higher density, and a non-porous structure. Also, the dense prills lack the clay or other coating found on the individual particles of regular porous prills. The problem, therefore, was to explore the sensitivity and detonation characteristics of various size fractions of dense prills, and attempt to relate these properties to some basic features of grain burning.

2. Importance of the study. The ultimate in design of a dense prilled AN-fuel mixture would be one in which a high density was achieved in combination with a reasonable order of sensitivity. This might be possible with a polymodular mixture, in which progressively smaller particles fill the interstices among those which are larger. The present investigation was considered a necessary and important preliminary to the study of such designs. A limitation was imposed because prill sizes in the general range of 50 to 1000 microns such as are required for this type of study are generally not those commonly manufactured in great quantity. The present investigation was thus limited to a lesser number of tests than would normally have been desirable.

CHAPTER II

REVIEW OF LITERATURE

A. CHARACTERISTICS OF AMMONIUM NITRATE

AN is the product of the reaction of ammonia and nitric acid. In the chemically pure state it occurs as colorless hygroscopic crystals which are relatively unstable. Some of the more important chemical characteristics follow: (Handbook, 1959; Taylor, J., 1959; Stites, et al, 1960b)

Formula: NH_4NO_3

Molecular weight: 80.05

Crystal forms: 5 or 6 forms, depending on temperature and pressure. The most important to this study are the forms III and IV, since with repeated cycling through the transition temperature between these forms (32.1°C) regular porous AN prills disintegrate.

Melting point: 169.6°C

Boiling point: slowly decomposes between 200°C and 260°C.

Specific gravity: 1.725 (form IV)

Solubility: 100 ml of water at 0°C will dissolve 118.3 gm of AN; at 100°C it will dissolve 871 gm. AN is also very soluble in alcohol, methyl alcohol, and ammonia. It is insoluble in ethyl ether, and in both aliphatic and aromatic hydrocarbons.

Decomposition reactions:

1. $NH_4NO_3 = NH_3 + HNO_3$ (endothermic)
2. $NH_4NO_3 = N_2O + 2H_2O$

3. $2NH_4NO_3 = 2N_2 + 4H_2O + O_2$ (evolves the most heat of all the reactions. This is the reaction in detonation)

4. $2NH_4NO_3 = N_2 + 2NO + 4H_2O$

5. $4NH_4NO_3 = 3N_2 + 2NO_2 + 8H_2O$

6. $8NH_4NO_3 = 5N_2 + 4NO + 2NO_2 + 16H_2O$

7. $5NH_4NO_3 = 4N_2 + 2HNO_3 + 9H_2O$

8. $4NH_4NO_3 = 2NH_3 + N_2 + NO + 3NO_2 + 5H_2O$ (endothermic)

Grades: Chemically pure (crystalline and granular)

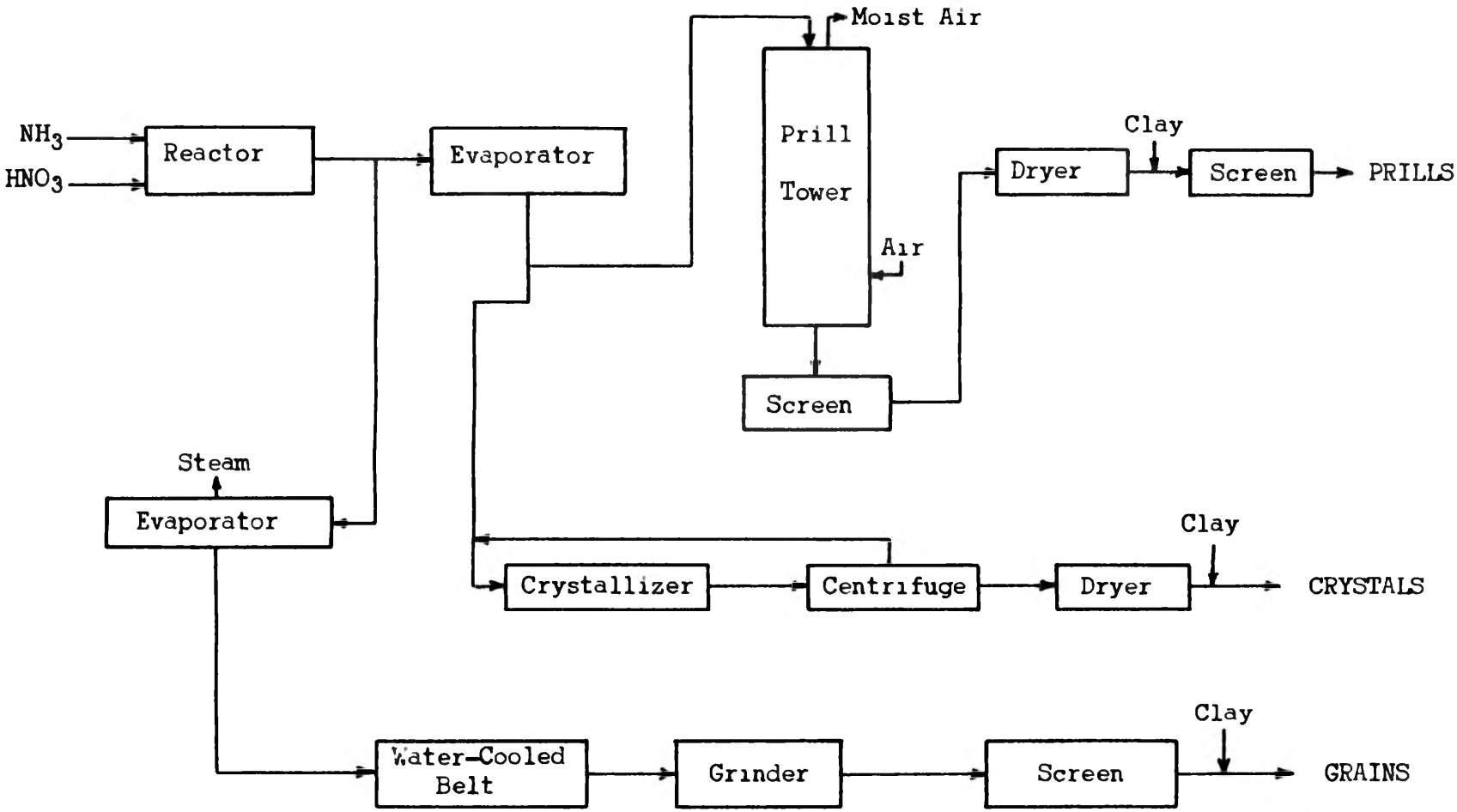
Technical (granular - 98 to 100 percent pure)

Fertilizer or conditioned (93 to 96 percent containing 32.5 to 33.5 percent nitrogen)

B. METHODS OF PRODUCING AMMONIUM NITRATE

In general, there are 4 methods of making ammonium nitrate. Three of the methods are shown on the flow diagram, Figure 1. From the top to bottom, the products are from the prilling, continuous vacuum crystallization, and Stengel processes. A fourth method, known as the grainer or high-pan process, is not used to any great extent in the fertilizer industry (Faith, et al, 1957). Since this investigation deals with a product from a particular manufacturing process, that of prilling, this will be examined more closely.

The typical fertilizer grade prill is produced by spraying molten AN with 4 to 5 percent moisture in a tower through a countercurrent flow of cool air (Ross, et al, 1945; Sauchelli, 1960). Liquid droplets congeal in their fall to form sphere-shaped particles of a size dependent upon the characteristics of the spray nozzles. The regular porous fertilizer grade AN prill is in the 8/20-mesh size range, or approximately 0.033 to 0.094 inches in diameter. As these congealed granules reach the bottom of the



PRODUCTION OF

AMMONIUM NITRATE

FIGURE I

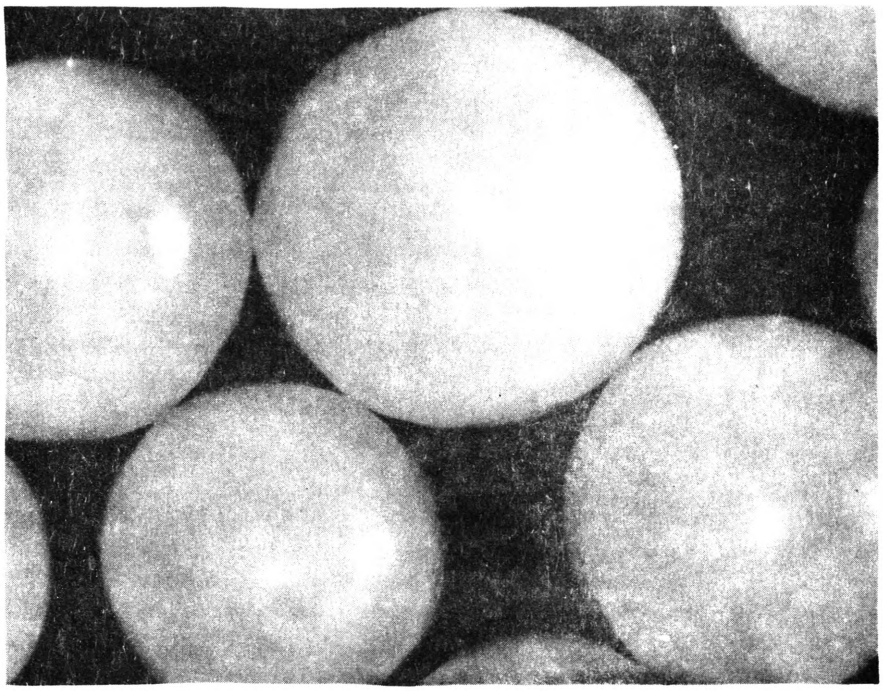
tower, they are collected in a hopper and are then conveyed on a belt to the drying equipment. When the 4 to 5 percent moisture is removed, a porous, roughly spherical particle results.

In the manufacture of dense prills, the process is changed to provide for the removal of moisture from the ammonium nitrate melt before entering the prilling tower. The result is a dense sphere of a certain size range depending upon the nozzles used in the spraying. Typical dense prills are shown in Figure 2. It can be seen that they are spherical and possess a smooth, non-porous surface. Other changes are also made in the manufacture of the dense prill which differentiate it from the regular product. In the product examined in the present investigation, the AN is phase-stabilized in order to change the temperature of transition from the usual 32.1°C. Also, since the dense prills are non-caking, there is no clay or other coating added to the surface.

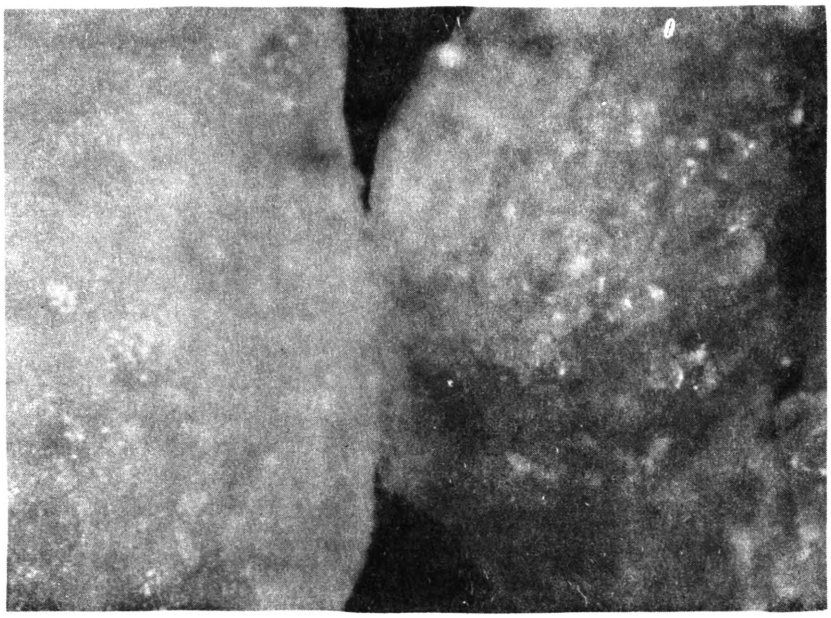
C. THE PHENOMENA OF DETONATION

Detonating explosives are those in which a chemical reaction is sustained by a shock wave which passes at a very high speed through the explosive. This is in contrast to deflagrating explosives which react with the oxygen contained in their compositions and are relatively slow in action. The speed of the detonation shock wave, the pressures developed, the resultant gas composition and volume, and other quantities are calculable from the thermohydrodynamic theory described by Cook (1958b), Eyring, et al, (1948) and Taylor (1952). A concise explanation of the principles for the solution of an explosive problem by the use of the thermohydrodynamic theory has been written by Clark (1959).

1. Ideal detonation. This is a detonation which proceeds at a rate which corresponds to the theoretical maximum velocity or the hydrodynamic



Typical Dense Prills (About 70x)



Cross-Section of Dense Prill, L., and

Regular Porous Prill, R. (About 200x)

AMMONIUM NITRATE PRILLS

FIGURE 2

value. It is a steady rate reached in a sufficiently large diameter charge and far enough away from the point of initiation that further increase in either factor will not cause an increase in velocity. The charge diameter and travel distance necessary to fulfill the conditions are functions of the characteristics of the explosive in question and vary with explosive composition. Such characteristics might be chemical composition, grain size (if granular), density, percent pore space, intimacy of mixing, confinement, or a number of other properties.

2. Non-ideal detonation. This refers to a steady velocity, attained in a charge of several diameters, that is lower than the ideal velocity. It is related to the rate of conversion of the explosive into its detonation products with accompanying lateral heat and pressure losses. There are four well-known theories of non-ideal detonation, known as the Nozzle (Jones, 1947), Curved Front (Eyring, et al, 1949), Geometrical Model (Cook, 1958b), and Variable Reaction Zone Length (Hino, 1959) theories. The various theories have been applied to AN-fuel oil mixtures, without any particular success (Yancik, 1960b).

D. SENSITIVITY AND THE INITIATION OF DETONATION

The methods of initiation and transmission of an explosive wave are not well known, although there have been many theories advanced on the subject. All agree on the necessity of the production of heat at the wave front. In the case of AN, it is proposed by Anderson, et al, (1958) that heat first liquifies, then vaporizes the material into gaseous ammonia and nitric acid.

The following are possible mechanisms for initiation in an explosive material (Bowden, et al, 1956):

1. Heating the explosive material to ignition temperature.
2. Adiabatic heating of the included gas spaces.
3. Formation of frictional hot spots
    a. on confining surfaces.
    b. on grit particles.
    c. between crystals of the explosive itself.
4. Viscous heating at high rates of shear.
5. Plastic deformation of the sharp point of a crystal.
6. Mutual reinforcement of gentle shock waves.
7. Ultrasonic vibrations.
8. Light of sufficient intensity.
9. Electrical discharge.

Experiments by various groups have shown the preceding mechanisms to be effective. Even in liquids it has been shown that initiation begins with heat produced in highly compressed air bubbles.

Cook (1958b) explains initiation of detonation as a heat-balance problem. Since explosive decompositions are exothermic by nature and create gaseous products, they tend to produce high pressure gradients and thereby intense shock waves. If the temperature produced in the shock front is high enough, detonation results.

In a granular explosive it is believed that some form of grain burning or surface decomposition occurs. The idea has been advanced that each contact point between grains could be a center of production of heat (Eyring, et al, 1948). Or, grains may be uniformly heated to ignition temperature over all or part of their surface by the impact of streaming particles ahead of the detonation wave front. The fact that sensitivity increases with an increase in free surfaces within the explosive is significant in that it shows that some form of surface ignition is in

operation. In propellant studies it has been found that cracked or otherwise defective grains are very likely to detonate rather than deflagrate. In the same studies it was found that whether pores were connected or non-connected was significant to sensitivity, the material possessing connected pore space being much more likely to detonate (Amster, et al, 1960).

For very small grains, where the ratio of surface area to volume is high, the percent of the surface ignited of each grain can be much lower than with larger grains to achieve the same sensitivity. It is found that the finer the grain size, the greater the sensitivity (Clark, et al, 1961b).

E. PREVIOUS RESEARCH ON PRILLED AN-FUEL MIXTURES

A considerable amount of research, both of practical and theoretical nature, has been done on regular porous prill-fuel oil mixtures. Numerous articles have been written in the technical journals concerning field experimentation, references to which may be found in the bibliography. The various symposia on mining research held at the Missouri School of Mines in recent years have contributed greatly to the literature on these mixtures. References to these papers may also be found in the bibliography.

Since 1957 the Missouri School of Mines has been actively engaged in research on AN-fuel mixtures. This research has been financially supported by the Monsanto Chemical Company of St. Louis, Missouri. Blasting is done at a testing area at nearby Fort Leonard Wood. The results of this program have been reported in the Ph.D. dissertation by Yancik (1960b), and the Master's theses by Kohler (1959) and Warga Dalem (1958). The following summary is compiled from these sources.

The explosive properties of ammonium nitrate-fuel blasting agents have been investigated by measurement of detonation velocity and sensitivity. Investigations were carried out on various mixtures of AN-fuel and certain parameters held constant while others were changed. Some examples of the parameters investigated are charge diameter, type and percent of fuel, charge density, particle size, type of confinement, percent moisture, and percent inert ingredients. It was found that regular prilled AN and no. 2 fuel oil, generally known as FO, had certain advantages over other types or forms of AN or fuels. These advantages were (1) low cost, (2) stability, (3) homogeneity, (4) relatively high energy yield, (5) practical level of sensitivity, and (6) availability and safety.

It was found that with porous prills, positive mixing of the AN and fuel oil could increase the detonation velocity as much as 800 feet per second. Maximum efficiency and sensitivity were achieved when the material was oxygen balanced, that is, containing about 5.5 percent by weight of fuel oil. Too little oil was found to be more detrimental than too much.

With respect to charge diameter and confinement, it was found that a steel casing gave a detonation velocity about 2000 feet per second higher than a clay charge casing of equal mass. The steel casing, in fact, approximated a borehole in solid, hard rock. The detonation velocity of the balanced mixtures increased with charge diameter, but even at an 8-inch confined diameter and 10-inch unconfined diameter the velocity was still more than 1500 feet per second below the ideal rate. The optimum diameter extrapolated from velocity-diameter curves was about 18 inches for steel confined charges, and 60 to 100 inches for those that were unconfined. Tests which allowed free air space to remain in loading the container showed a considerable decrease in detonation velocity. The

diameter below which detonation cannot be initiated (the critical diameter) was found to be 1½ inches confined and 4 inches unconfined. Detonation velocity was found to increase almost linearly with increase in density, if all other variables were held constant.

With the regular prilled AN-fuel oil mixtures, a reduction in particle size was found to increase both detonation velocity and sensitivity. Inert coatings, by holding oil to the grain surface more effectively, influenced an increase in the detonation velocity although decreasing the sensitivity. Organic coatings, however, greatly sensitized the material.

Repeated cycling through the 32.1 degrees Centigrade transition point was found to cause regular porous AN prills to become more sensitive to initiation. An increase in water content was found to decrease the detonation velocity, but did not significantly affect sensitivity. Beyond 8 to 10 percent water, however, detonation was impossible.

The porous structure of regular AN prills was believed to be the primary factor contributing to the excellent explosive properties. Apparently the pores not only allow fuel oil to more intimately contact the AN, but also serve as hot spots and therefore act as centers of initiation in each prill.

Research with dense ammonium nitrate prills has not been so extensive as with the porous variety. The total available literature consists of two papers by Clark, et al, (1961a, 1961b), and a chapter in the dissertation by Yancik (1960b).

Yancik based his conclusions on the investigation of 33 dense microprilled (size less than 20 mesh) products produced by varying the nozzle sizes used in the prilling tower. It was found that the explosive properties were controlled by the particle size distribution, which effect

was attributed to the influence of the varying number of grain contact points. The pouring density in a 6-inch diameter pipe was found to be 1.08 to 1.10 grams per cubic centimeter, and the detonation velocity to be 17,500 feet per second, or about 4000 feet per second higher than regular prilled AN under similar conditions. At larger than 8-inch confined charge, the dense microprilled mixture was found to behave as an ideal explosive. As with regular porous prills, sensitivity varied with oil content. However, the dense variety reached maximum sensitivity at one percent fuel oil. Confinement had the same effect as with porous prills, that is, the detonation velocity was higher in confined than in unconfined charges.

Clark related the variations in detonation velocity to the percentage of AN consumed in the reaction zone. By relating the particle size distributions of the 33 dense microprilled products listed in Yancik's thesis to the surface burning theory with constant reaction rate, he arrived at the empirical relation

$$D = 6600\ N^{0.21}$$

where D is the measured detonation velocity, and N is the percent of AN consumed in the reaction zone. This equation is a variation of that of Cook (1958b) for non-ideal detonation, which in the same form is

$$D = 1700\ N^{0.50}$$

Clark's equation predicts the detonation velocities found in AN more accurately than does the equation by Cook.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. DETONATION VELOCITY MEASUREMENTS

Since the velocity of detonation is the most readily measured performance parameter of an explosive which can be related to the theoretical calculations, this was measured for the dense microprilled AN-fuel oil mixtures. The equipment used is shown in Figures 3 and 4a, and consists of the following:

1. A 12-conductor cable with corks attached to the end of each wire. These are placed in accurately spaced holes in the charge container.
2. Pin mixer and protective box.
3. Cordin pin oscillograph and modified Tektronix 533 oscilloscope.
4. Hewlett-Packard oscilloscope camera with Polaroid back.

The operation proceeds as follows:

1. The explosive mixture to be measured is placed in the container (iron pipe) and properly primed.
2. Corks are introduced into their proper holes.
3. A high electrical potential is placed on the wires held in place by the corks.
4. The oscilloscope camera shutter is opened.
5. The primer and explosive charge is detonated, following which:
   a. The voltage on the upper cork wire crosses to ground via the ionization in the reaction zone, beginning a saw-tooth waveform on the oscilloscope. Simultaneously, the pin oscillograph places timing marks every 2 microseconds along the trace.

b. As the ionization travels on, it allows the voltage to flow from cork wire no. 2 to ground, creating a blip on the oscilloscope trace.

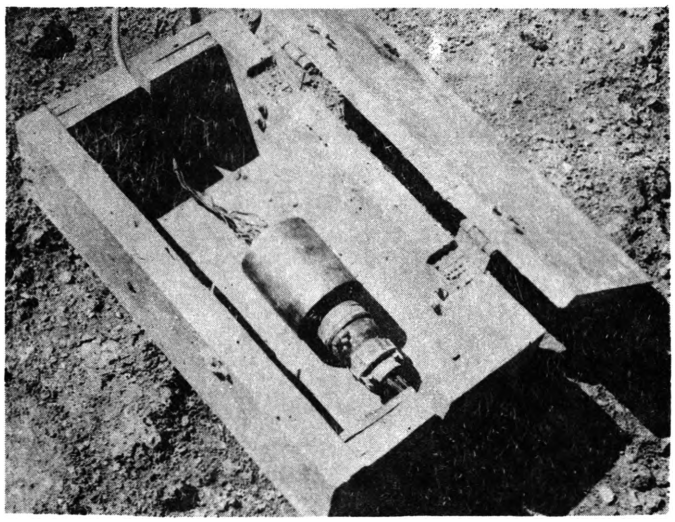
c. Step "b" is repeated for each cork wire until the charge has completely detonated.

6. The oscilloscope camera lens is closed and the film developed. A typical trace is shown in Figure 4b. A more complete description of equipment for the measurement of detonation velocity may be found in the thesis by Kohler (1959).

B. SENSITIVITY MEASUREMENTS

As stated in Section D of Chapter II, sensitivity is a parameter that is very difficult to predict. However, it is relatively simple to measure, and the system used with explosives is usually some sort of a "go, no-go" type. For this investigation 3-inch diameter pipe in either 2-foot or 1-foot lengths was used to confine the material to be tested. In the case of pipe of 1-foot length, 6 inch squares of 1/8-inch steel were used as witness plates beneath the base of each charge to insure evidence of detonation or non-detonation. With 2-foot pipe, witness plates were unnecessary since it was apparent from the crater when detonation took place. The most convenient primer to use in small amounts is the common blasting cap. For this study special no. 6 caps were used which had only the main charge present in the shell and had no ignition mixture or leg wires. Primers of any strength could then be made by simply tying a specific number of special caps to a regular electric blasting cap. Thus, figures for sensitivity are stated as the "number of caps required for detonation". In extremely insensitive mixtures where the sensitivity is over 50 caps, some other means of priming must be used to achieve

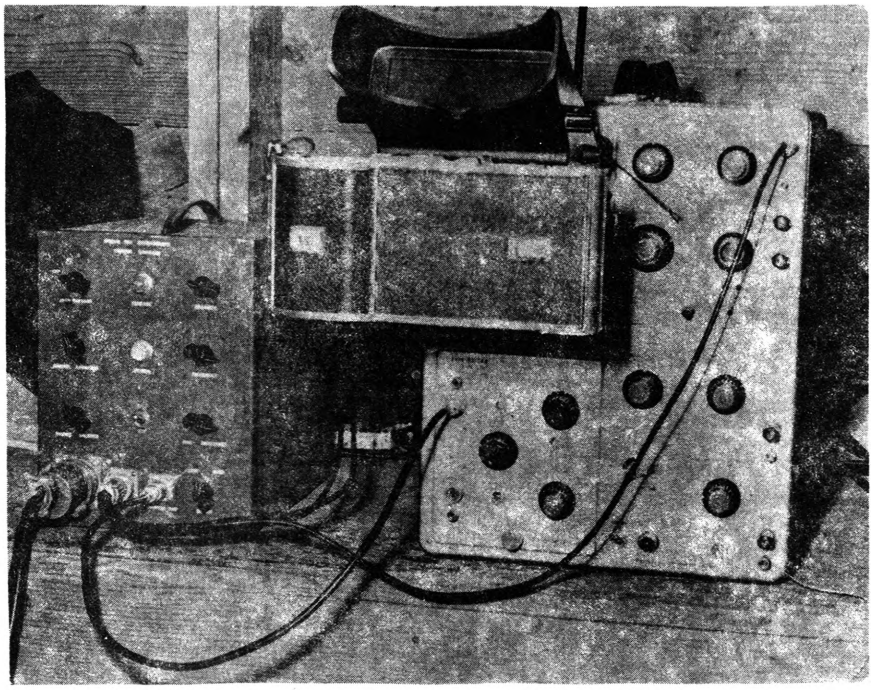
Charge container with cork pins and dynamite primer.



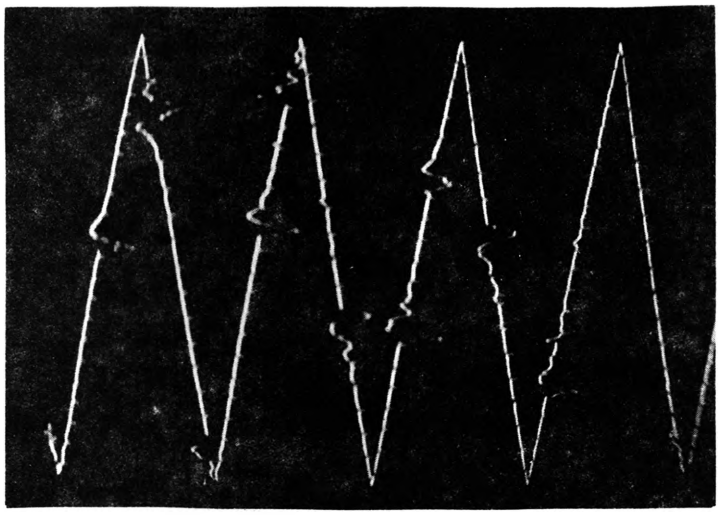
Pin mixer head and protective box.

DETONATION VELOCITY MEASUREMENT EQUIPMENT

FIGURE 3



a. Pin oscillograph, oscilloscope, and camera.



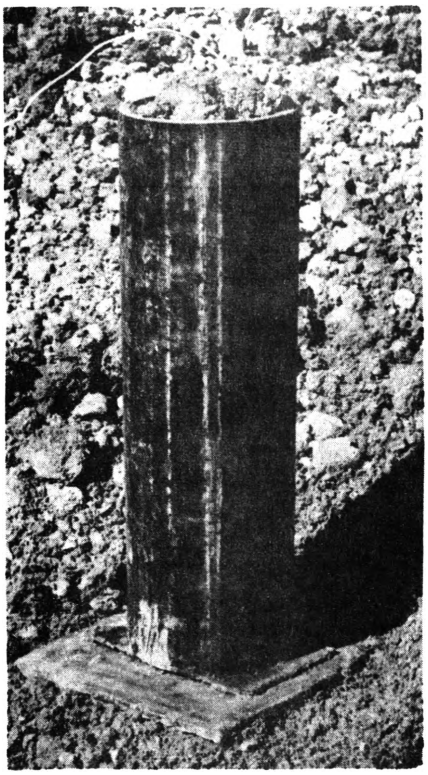
b. A typical oscilloscope trace record.

DETONATION VELOCITY MEASUREMENT EQUIPMENT

FIGURE 4

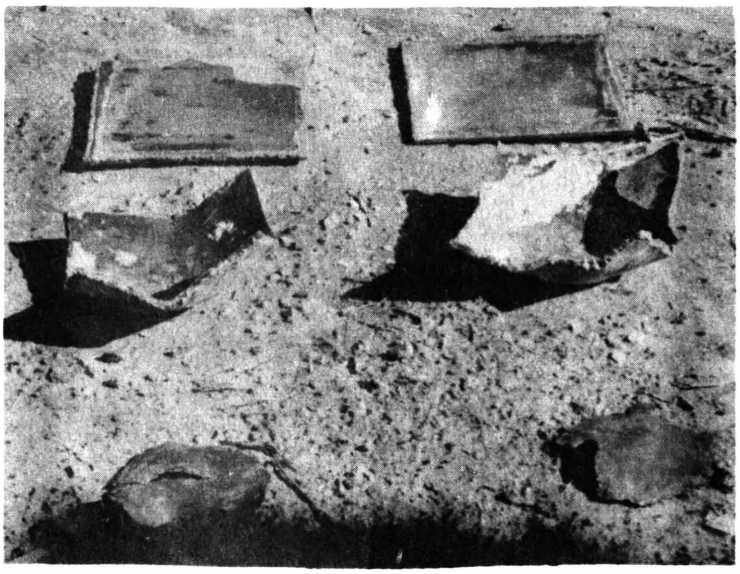
detonation.

Figure 5 shows a 1-foot sensitivity pipe and various witness plates.



Sensitivity Test Pipe

and Witness Plate



Witness Plates

Detonation results, top to bottom:

none, partial, and complete.

SENSITIVITY TEST EQUIPMENT

FIGURE 5

CHAPTER IV

DISCUSSION OF RESULTS

A. INVESTIGATION OF THE PHYSICAL PROPERTIES OF DENSE PRILLS

1. Determination of density. In order to determine the density of dense prilled ammonium nitrate a method of actual measurement of the individual spherical particles was utilized. A binocular microscope with a calibrated eyepiece was used for diameter measurements. The total volume for a large number of prills was then calculated, and the entire sample weighed on an analytical balance.

The material investigated was the Monsanto dense prilled product designated as "E-2" which has a size range of 8/20 mesh, or diameters of 2.38 to 0.84 millimeters. This product was chosen because its comparatively large size made it possible to obtain a sample of reasonable weight without the problem of measuring an extremely large number of prills. Samples were taken from various bags of material.

To determine if moisture drawn from the air was adding to the weight, a sample was heated at 101 degrees Centigrade in a constant temperature oven, then re-weighed after varying periods of time. It was found that the maximum weight loss was approximately $2\frac{1}{2}$ percent. Upon cooling for 1 hour, the loss was regained.

The average density of the dense prill of the size investigated was found to be 1.52 grams per cubic centimeter. A method of liquid displacement resulted in an average density of approximately 1.67 grams per cubic centimeter. However, with a liquid displacement method, any absorption by the prill will introduce an error in the determination by giving an apparently larger volume of voids. The calculations based on the results

of such a test will then give a higher density to the AN prills. For this investigation the value of 1.52 grams per cubic centimeter was accepted.

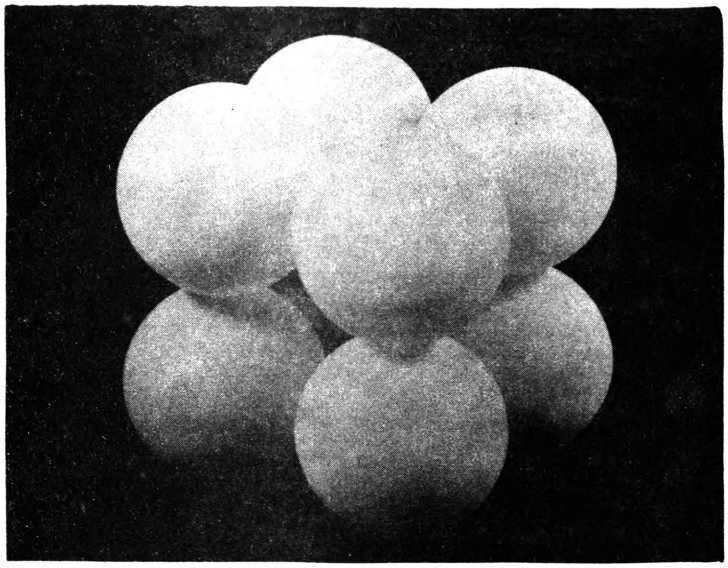
2. Determination of theoretical bulk density. Dense prills, being spherical, will fill a charge container in a manner that should follow the various spherical packing arrangements. When the density of the prills and the packing density are known, the packing arrangement can be determined.

The possible packing arrangements of spherical particles are well known, as long as only one particle size is being considered. With a mixture of many sizes, however, it becomes extremely difficult to determine what characteristics the packing will have. According to Dalla-Valle (1943, p. 5);

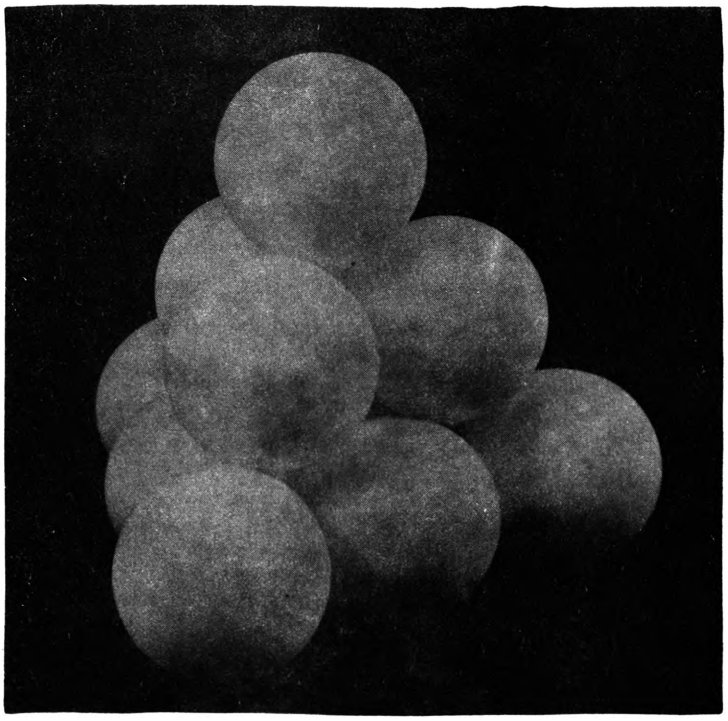
> "Packings are inherently very complex and there is still much to be learned about them. For example, we may pose the problem of how to select the proper sizes and the correct proportions of a given material so that the larger voids are filled with smaller particles, and these voids in turn filled with still smaller particles, and so on. Theoretically we should be able to obtain a very low percentage of voids in this way; nevertheless, both theoretically and practically this problem remains unsolved."

With spheres, the percentage of voids ranges from a maximum of 47.6 with a cubic packing to a minimum of 26.0 with a rhombohedral packing. These percentages are true only for spheres of uniform size. Figure 6 shows spheres in these characteristic packing arrangements.

By knowing the density of the individual prills, the maximum bulk density attainable may be calculated as follows: if a bulk density of 1.00, for example, is to be realized with 1.00 gram of AN-FO, the volume filled must be 1.00 cubic centimeters. However, the AN prills were found to have a density of about 1.52 grams per cubic centimeter, which should result in 1.00 cubic centimeter of material weighing 1.58 grams,



Cubic



Rhombohedral

SPHERE PACKING ARRANGEMENTS

FIGURE 6

including fuel oil weight. Therefore, there must be

$$1.00 - \frac{1.00}{1.58} \times 100, \text{ or } 36.7 \text{ percent voids present.}$$

Percent void was calculated for other bulk densities, and the results plotted as shown on Figure 7. It is apparent from the figure that the maximum density theoretically possible with a uniform size should be 1.17 grams per cubic centimeter. The variation in size of each screen fraction as shown in Table I, plus the improbability of perfect rhombohedral packing, will cause variation in the maximum bulk density attainable.

3. Determination of the specific surface of dense prills. Specific surface, S, defined as the total surface of a unit weight of material, depends only upon the average diameter, d, and the density, ρ, when referring to spherical particles. The relationship is as follows:

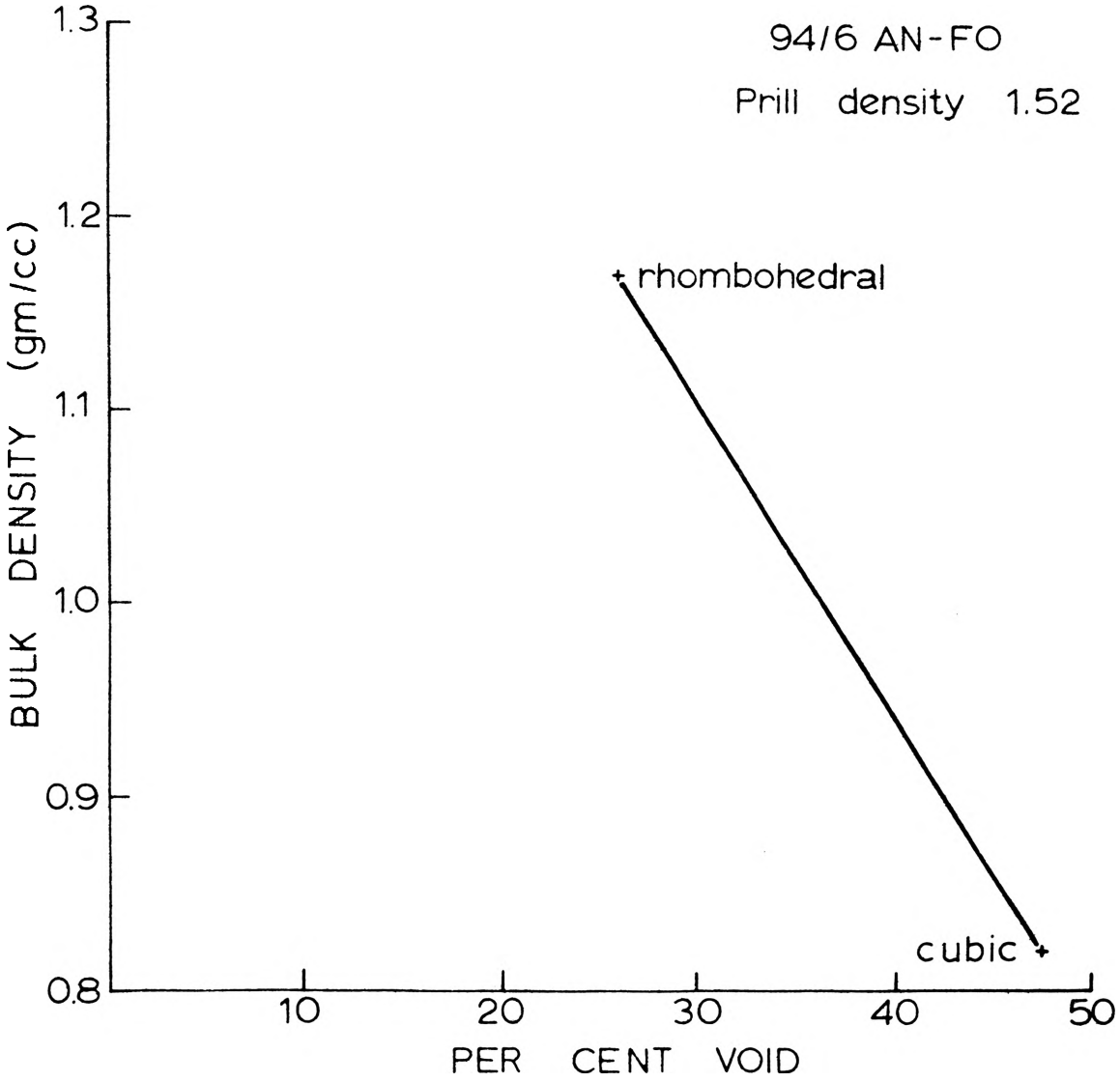
$$S = \frac{6}{\rho d}$$

Since dense ammorium nitrate prills have a spherical shape, and in the preceding section the determination of density was discussed, we are justified in calculating the specific surface of the various size fractions encountered in this study. Table I and Figure 8 show the results of these calculations.

B. DETONATION VELOCITY TESTS

The detonation velocity of the dense prilled ammonium nitrate described in the preceding sections was investigated by the methods described in Chapter III. The Monsanto Chemical Company, supplier of the AN, designates the prills as "E-2" or "E-3" depending upon the size distribution.

The number of tests was limited due to the difficulty in acquiring dense prilled material in the required size ranges. Grinding of dense prills would have provided the correct sizes, but the particles would no



PER CENT VOID vs BULK DENSITY WITH UNIFORMLY SIZED PRILLS

FIGURE 7

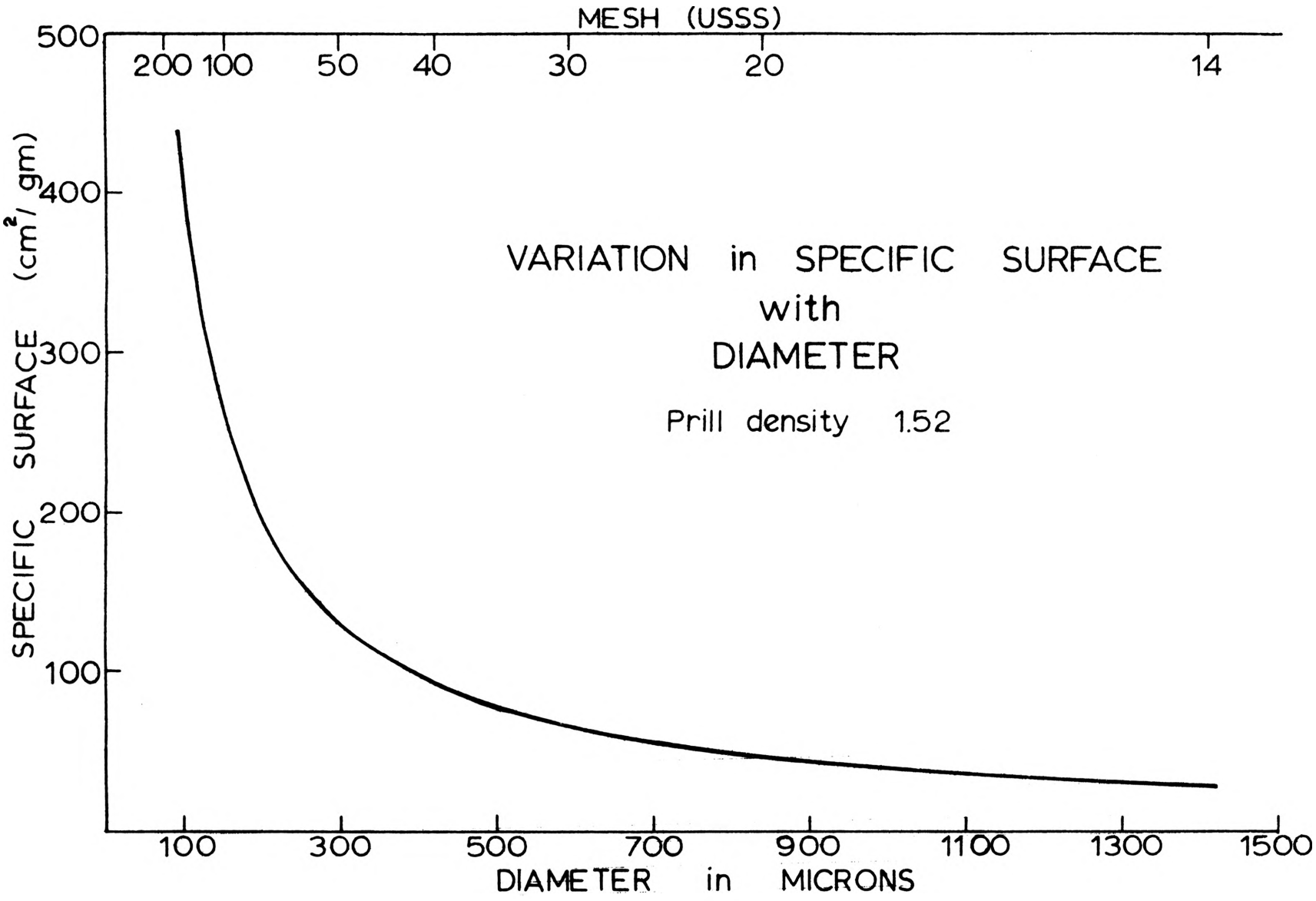

MESH (USSS)
500
200 100 50 40 30 20 14
400
300
200
100
SPECIFIC SURFACE (cm²/ gm)
VARIATION in SPECIFIC SURFACE
with
DIAMETER
Prill density 1.52
100 300 500 700 900 1100 1300 1500
DIAMETER in MICRONS

FIGURE 8

TABLE I

CHARACTERISTICS OF SIZE FRACTIONS TESTED

Mesh Size (USSS)	Diameter (microns)	Average Dia. (microns) (1)	Percent Size Variation (2)	Specific Surface (sq cm/gm)
8/20	2380-840	1520	101.3	26.0
12/20	1680-840	1260	66.7	31.3
20/30	840-590	715	35.0	55.2
30/40	590-420	505	33.7	78.1
40/50	420-297	359	34.3	110
50/60	297-250	274	17.2	144
60/80	250-177	213	34.3	185
80/140	177-105	141	51.1	280
140/200	105-74	90	34.4	439
-200	74-	37	200	1067

(1) Average diameter is a simple arithmetic mean of diameter limits except in the case of 8/20 where it is the statistical result from a screen analysis.

(2) Determined by relation of particle sizes

$$\frac{\text{large} - \text{small}}{\text{average}} \times 100$$

longer have been spherical in shape. Again because of a lack of material in quantity, each fraction was tested only at the density achieved by rapping the velocity test pipe gently a few times after filling.

Regardless of the testing density, the detonation velocity may be related to that at any other density by the equation (Cook, 1958b),

$$D^* = D^*_\rho + M^*(\rho_1 - \rho)$$

where D^*_ρ is the detonation velocity at the density ρ and M^* is the slope of the ideal velocity-density curve. The density ρ_1 is that to which it is desired to correct the detonation velocity. The equation is then solved for D^*. This straight line relationship holds true in the density ranges of this study. All detonation velocities were corrected to a density of 1.0 grams per cubic centimeter for comparison with one another.

In order to initiate the mixtures, it was found that a primer consisting of 4-half sticks of 1¼ by 8 inch, 60-percent ammonia dynamite was sufficient for initiation of all but the larger sizes of prills. With the 8/20 and 12/20 mesh fractions, a primer of greater strength such as the military composition C-4 was necessary for dependable initiation.

The field test data are listed in the Appendix. Correction was made to a density of 1.0 grams per cubic centimeter and the results shown in Table II. A digital computer was used to fit a curve to the corrected data by the method of least squares. The result was that a third degree polynomial equation gave the best fit. The equation is as follows:

$$D = 18.2 \times 10^3 - 13.4d + 18.0 \times 10^{-3}d^2 - 87.7 \times 10^{-7}d^3$$

where D represents the detonation velocity in feet per second, and d represents the prill diameter in microns. If the particles in the 8/20 mesh range are not considered, the points may be represented by the straight line,

TABLE II

CORRECTED DETONATION VELOCITY TEST RESULTS
density = 1.0 gm/cc

Mesh Size (USSS)	Average Diameter (microns)	Detonation Velocity (ft/sec)
8/20	1520	8,520
"	"	8,510
"	"	8,760
12/20	1260	12,700
"	"	12,380
20/30	715	14,420
30/40	505	14,880
"	"	14,490
"	"	14,160
40/50	359	15,700
"	"	15,400
50/60	274	16,220
60/80	213	16,210
"	"	16,170
80/140	141	16,460
"	"	16,540
140/200	90	16,850

$$D = 16{,}900 - 3.60d$$

These curves and the corrected experimental points are plotted on Figure 9.

Most investigators agree with Eyring, et al, (1949) that detonation in granular explosives begins at the grain surface and burns toward the center in a layer by layer manner. Using this assumption, and also assuming the reaction zone to be of constant length if the diameter of the charge container is unaltered, then a relation should exist between the grain size of the explosive and the percent of material consumed in the reaction zone.

This relation has been considered by Clark, et al, (1961b) with reference to polymodular dense prilled AN-FO mixtures, and Cook (1958b) with reference to most non-ideal explosives. The empirical equations, considering the same velocity at 100 percent agent consumed, are as follows:

Clark: $D = 6600\ N^{0.21}$

Cook: $D = 1736\ N^{0.50}$

In each equation, D is the detonation velocity in feet per second and N is the percent of the agent consumed in the reaction zone. Cook (1958a) states that although his equation is based on granular explosives in which the grains are homogeneous in composition, it conforms to the binary AN-FO systems because of the nearly uniform distribution of oil throughout the AN prills. This is approximately true in reference to regular porous prilled AN, but does not apply to the dense prilled product. It is evident from visual examination of any large-grained, dense AN-FO mixture that the oil is not distributed throughout the prill, but is concentrated on the surface. With smaller prills this concentration upon the prill surface is not as apparent, due to the much greater surface area available for distribution of the oil.

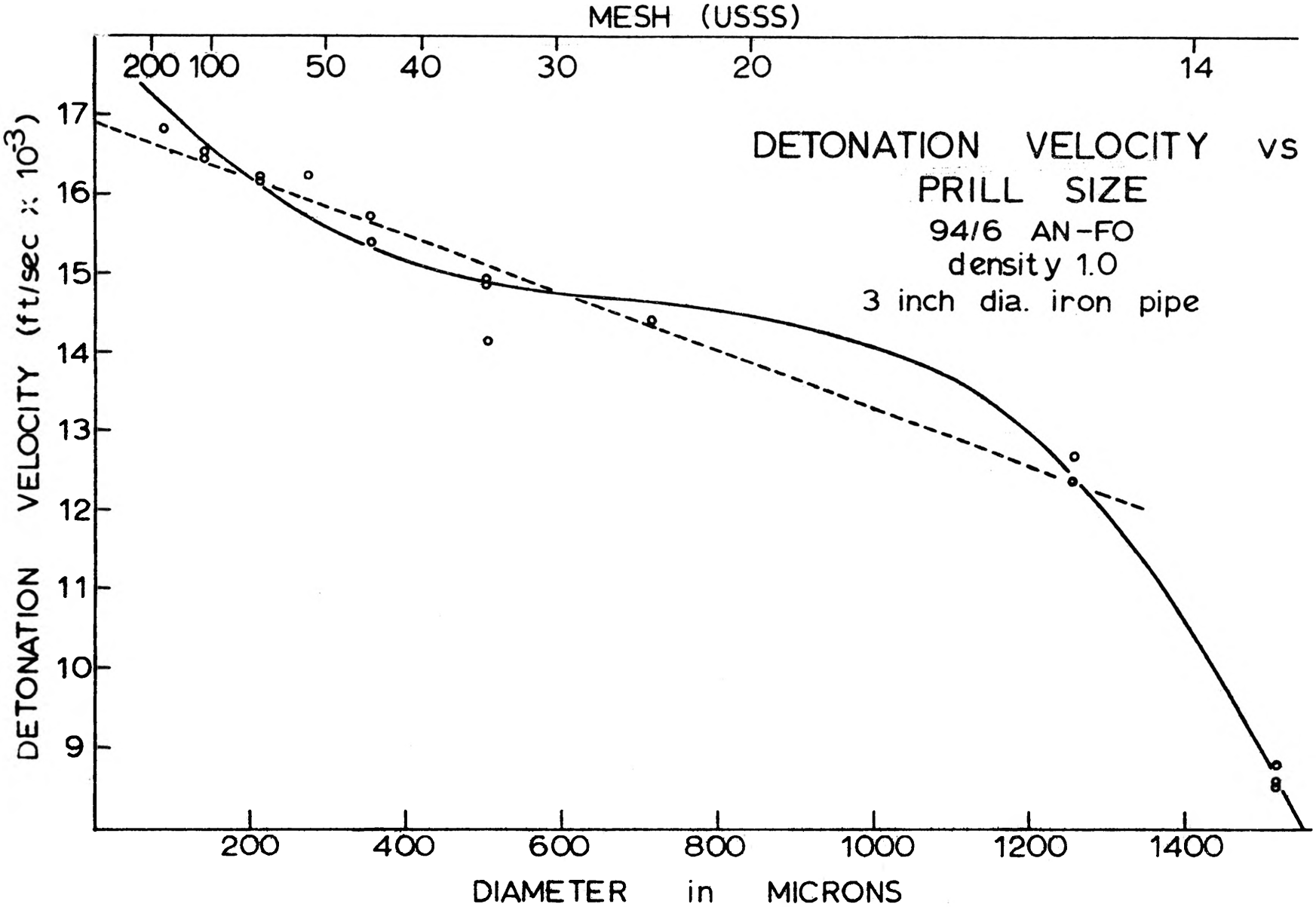
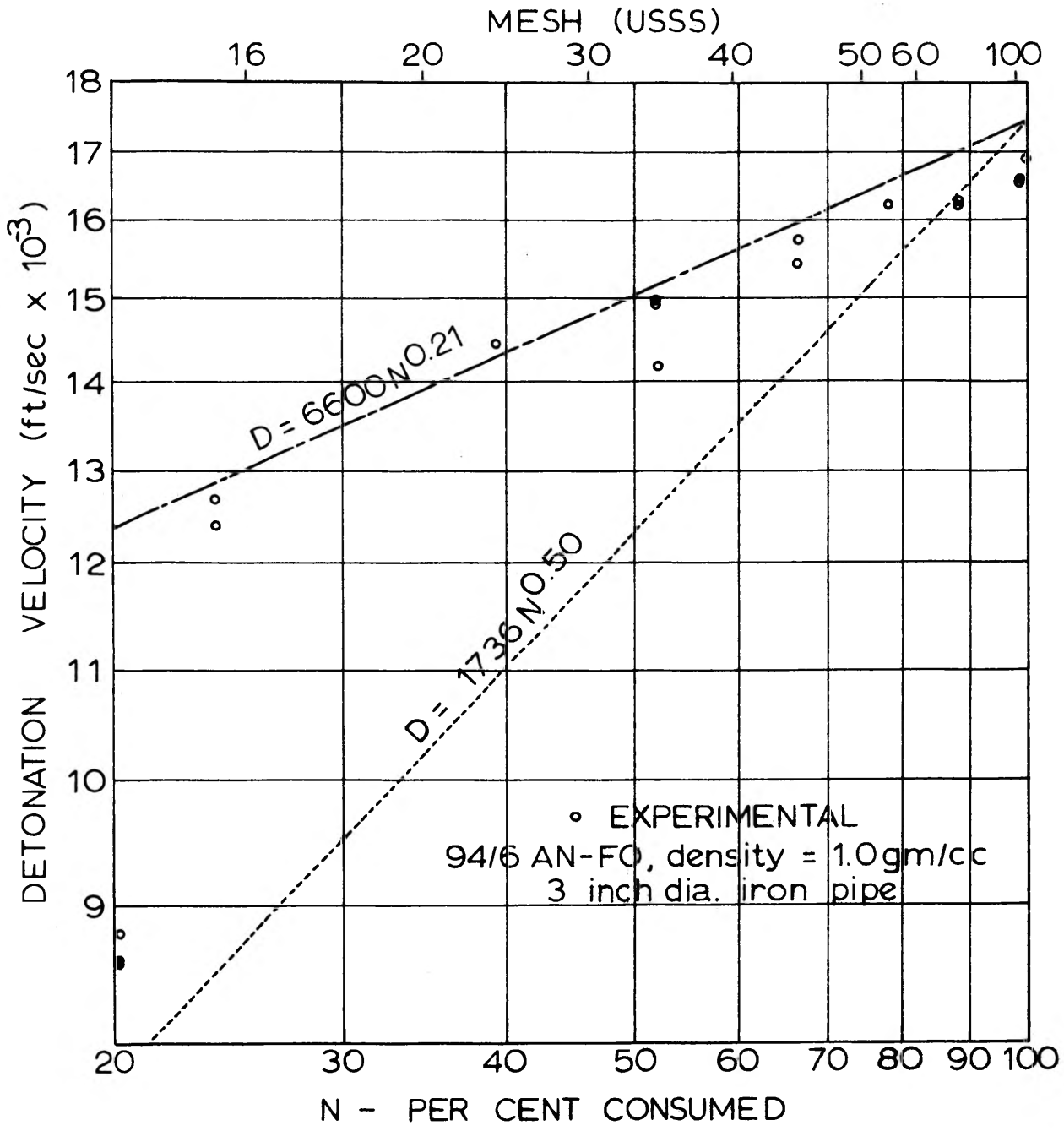

MESH (USSS)
200
100
50
40
30
20
14
DETONATION VELOCITY vs
PRILL SIZE
94/6 AN-FO
density 1.0
3 inch dia. iron pipe
DETONATION VELOCITY (ft/sec x 10^{-3})
17
16
15
14
13
12
11
10
9
200
400
600
800
1000
1200
1400
DIAMETER in MICRONS

FIGURE 9

In order to determine the extent to which either Clark's or Cook's equation could be correlated with the experimental data, the percent consumed, N, was calculated for each size fraction tested. It was assumed that ignition was initiated over the complete surface of the grain and combustion proceeded toward the center at a constant rate. Figure 10 shows the results of calculations considering complete consumption of a 110-micron diameter grain in the reaction zone as compared with the curves of Clark and Cook. It can be seen that the equation by Clark predicts more closely the actual detonation velocities found with the dense prilled AN-FO mixtures. The points falling near the 20 percent axis represent the large particles in the size fraction 8/20 mesh.

Possible factors influencing the decrease in detonation velocity with increase in size between the 1260 and 1520-micron diameter particles were examined. It was considered that since grain burning was taking place from the surface inward, and since fuel oil remains on the surface of the grain after mixing, there might be an extremely oxygen-negative condition decreasing the detonation velocity of the large particles. Since the amount of AN consumed is calculated to be approximately 20 percent with the 8/20 mesh size, the oxygen balance that results with complete fuel oil consumption is minus 4.15 gram atoms per 100 grams of mixture. The amount consumed of the 12/20 mesh size prill was calculated to be 24 percent; for this size the oxygen balance is minus 3.49. The next smaller size had a calculated amount consumed of 39 percent, giving an oxygen balance of only minus 1.90 gram atoms per 100 grams of AN-FO. Another factor which may influence detonation velocity within the size range of 8/20 to 12/20 mesh is that the critical diameter of the AN-FO is closely approaching the 3-inch pipe diameter. This, combined with the highly



RELATION BETWEEN DETONATION VELOCITY AND PERCENT OF EXPLOSIVE CONSUMED IN THE REACTION ZONE

FIGURE 10

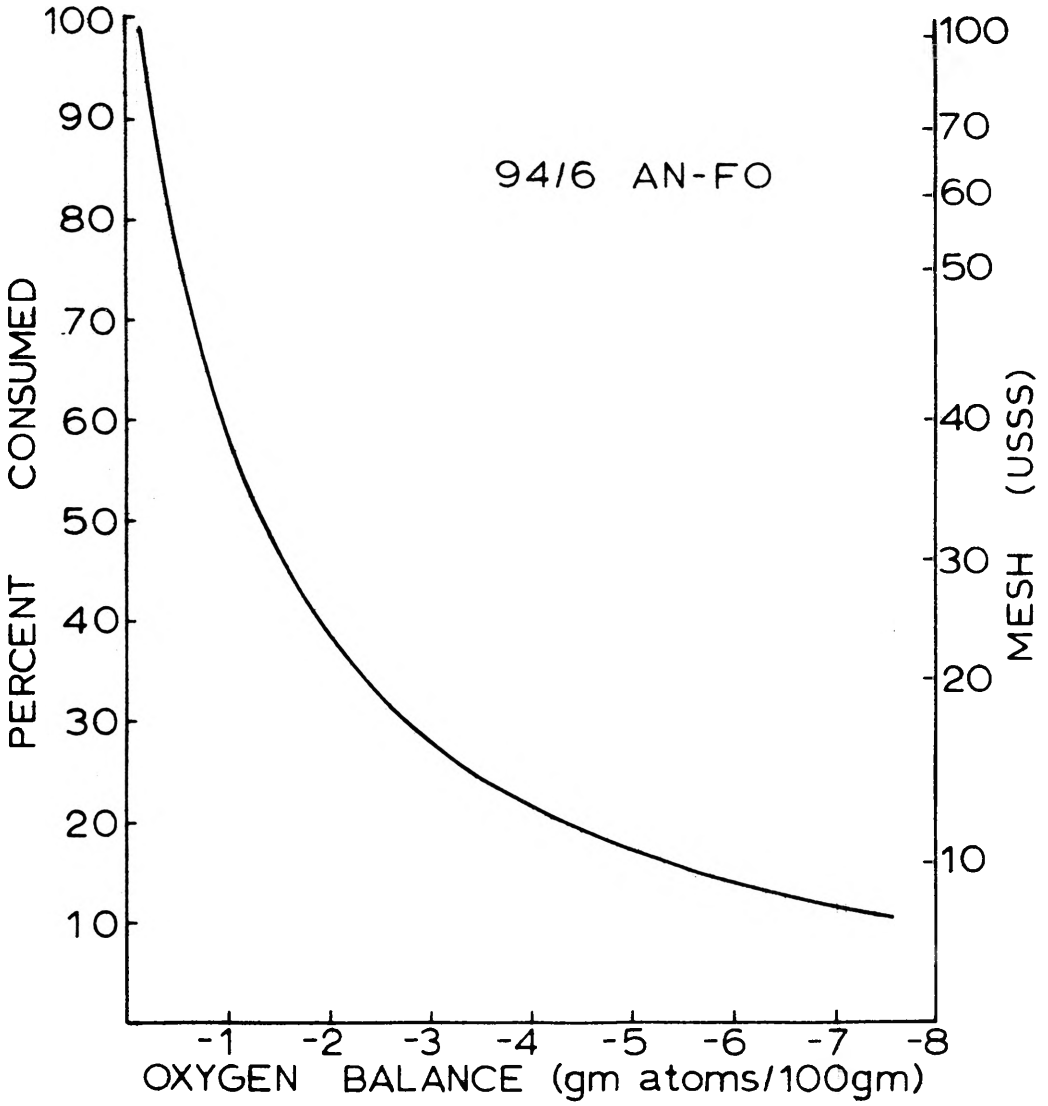
negative oxygen balance, could cause the observed lowering of the detonation velocity. Figure 11 shows how the calculated oxygen balance becomes more negative as the percent of explosive consumed decreases.

Ideal curves relating detonation velocity to density and fuel oil content may be found in the Appendix. The program used for the calculation of these parameters was written primarily for near oxygen balanced conditions: therefore, in the fuel oil content curve there may be some error toward the more negative end of the oxygen balance axis.

C. SENSITIVITY TESTS

In order to determine the sensitivity of the various size fractions of dense prills, the procedure described in Chapter III was utilized. For determination of relative sensitivity it is desirable that the loading density of all fractions tested should be the same, or very nearly so. However, as stated previously, the smaller sizes have a very low loading density. It was felt that it would be more undesirable to press-pack the material in order to achieve a higher density, than it would be to simply test at the density attained by uniform vibration of each size. With the 30/40-mesh size, this procedure resulted in a density of over 1.0 gram per cubic centimeter. Table III shows the results of sensitivity determinations on the various size fractions.

Relationships between the experimental data and physical parameters of the individual prill sizes were examined. It was found that there was a definite relationship between the number of prills contacting the primer for each size fraction. For example, the number of prills of size 140/200 mesh that contact the surface of the minimum primer (1 cap) is nearly the same as the number of 20/30 mesh prills contacting the minimum primer (40 caps) for that size. The intermediate sizes also followed this



PERCENT OF EXPLOSIVE CONSUMED IN THE REACTION ZONE vs OXYGEN BALANCE

FIGURE 11

TABLE III

SENSITIVITY TEST MEASUREMENTS

Size, USSS Mesh	Density, gm/cc	Minimum Primer*
8/20	1.04	over 50 caps
12/20	1.00	over 50 caps
20/30	1.00	40 caps
30/40	1.07	35 "
40/50	1.01	10 "
50/60	0.94	8 "
60/80	0.86	3 "
80/140	0.83	2 "
140/200	0.71	1 "
-200	0.73	2 "

* 3 inch diameter iron pipe.

relationship. Figure 12 shows this relationship and the cap sensitivity. For calculation of the number of prills contacting the surface, the prills were considered to be in the most open packing and the cap bundle was considered to be without voids. These assumptions are believed to be valid, since only a relative comparison was desired. Each cap, for calculation, was considered to occupy an area of 0.067 square inches.

The upper and lower limits for the number of prills contacting the primer on Figure 12 were arrived at by considering the sensitivity range to be ± 5 caps for the more insensitive mixtures, ± 2 caps for intermediate sensitivities, and ± 1 cap for the most sensitive mixtures. The limits for the one-cap sensitive mixture were not plotted since the lower limit would have been zero and the upper limit off the graph.

The most reasonable explanation for the relationship that was found appears to be that the contact points between the primer and the prills act as hot-spots in accordance with the theories of Eyring, et al, (1949), Bowden and Yoffe (1952), and others. The relative amount of surface area exposed to the heat from the primer appears to have only secondary effect upon the sensitivity.

The size fraction minus 200 mesh is not plotted on the graph because no detailed particle size distribution was made on that material. The reason for the anomalous sensitivity found with this fraction was not discovered.

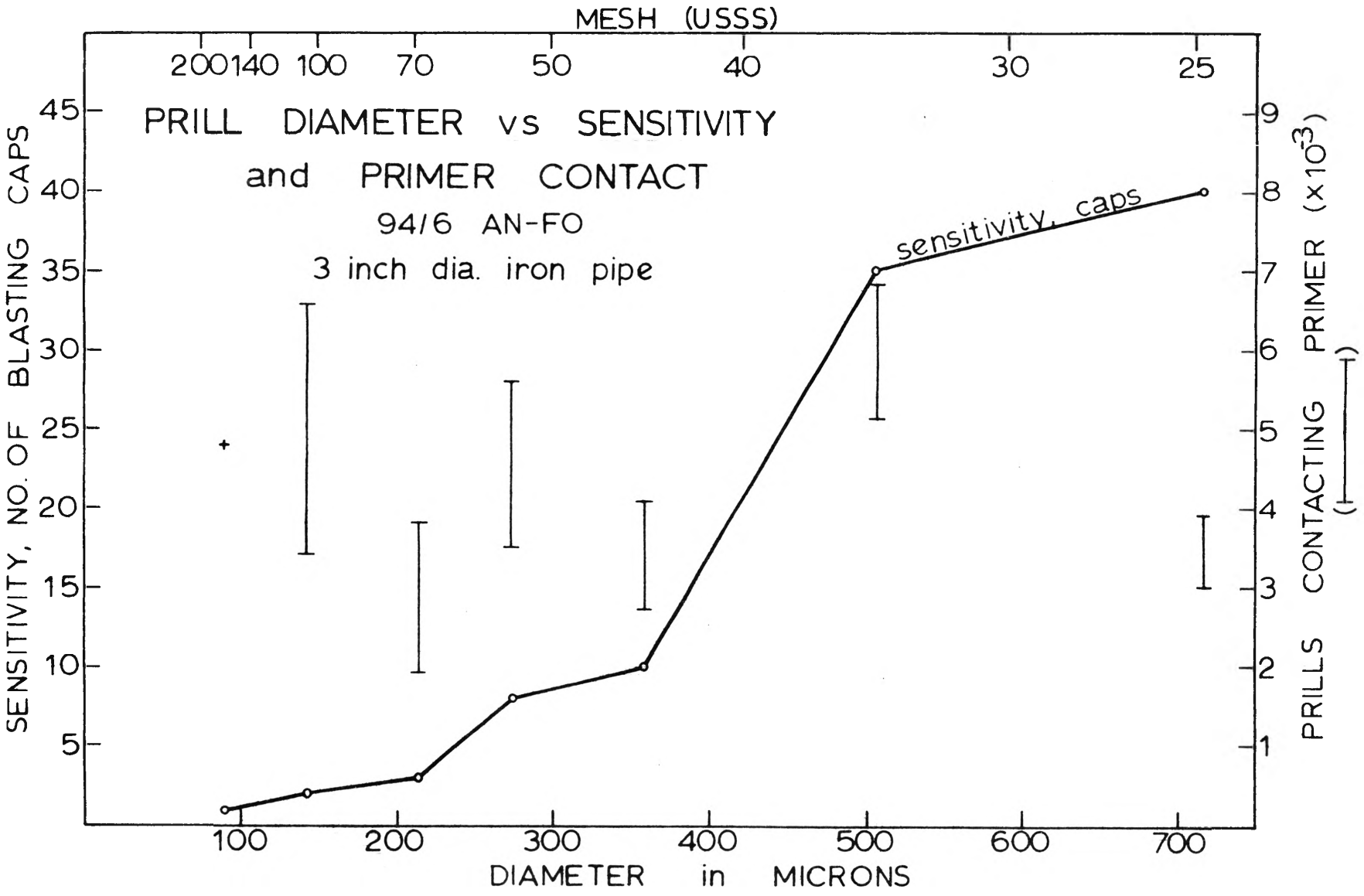

MESH (USSS)
200 140 100 70 50 40 30 25
PRILL DIAMETER vs SENSITIVITY
and PRIMER CONTACT
94/6 AN-FO
3 inch dia. iron pipe
sensitivity, caps
SENSITIVITY, NO. OF BLASTING CAPS
PRILLS CONTACTING PRIMER (x10⁻³)
45
40
35
30
25
20
15
10
5
9
8
7
6
5
4
3
2
1
100
200
300
400
500
600
700
DIAMETER in MICRONS

FIGURE 12

CHAPTER V

CONCLUSIONS

With dense ammonium nitrate prills it was possible to predict the maximum loading density that could be attained by close packing with the larger sizes. Dense prills were not in sufficient supply, however, to allow testing of the explosive properties of each size fraction at various loading densities. It is believed that with the small prills there might be such a high ratio of surface friction to mass that they are not readily rearranged into a closer packing after pouring.

The detonation velocity results with the various size fractions show that Clark's equation, derived from a study of polymodular distributions of dense prilled AN, predicts closely the actual behavior of the dense prilled mixtures with discrete particle size fractions. In the largest size tested (8/20 mesh), which is far from the range with which Clark worked, his equation does not apply in the 3-inch diameter pipe. However, these fractions, being so difficult to initiate, would seem to have little application as blasting agents. Part of the variation in velocity might be due to a very oxygen-negative condition existing in the percent of the blasting agent consumed in the reaction zone.

Sensitivity tests showed the expected general decrease in sensitivity with increase in size. The minimum primer ranged from 1 cap with the 140/200 mesh size to about 400 grams of a commercial cast primer or the plastic military composition C-4 with the 8/20 mesh size. A correlation was found in the case of blasting cap primers between the number of calculated contact points between the blasting agent and the minimum primer. Approximately 4000 to 5000 contact points exist regardless of the size in

question, up to the 20/30-mesh size fraction. It may be found that with polymodular AN-FO mixtures one could predict the sensitivity by estimating the number of prills in a unit plane section and relating this to the cap cross sectional area. No correlation was found between specific surface of prills and the sensitivity or detonation velocity.

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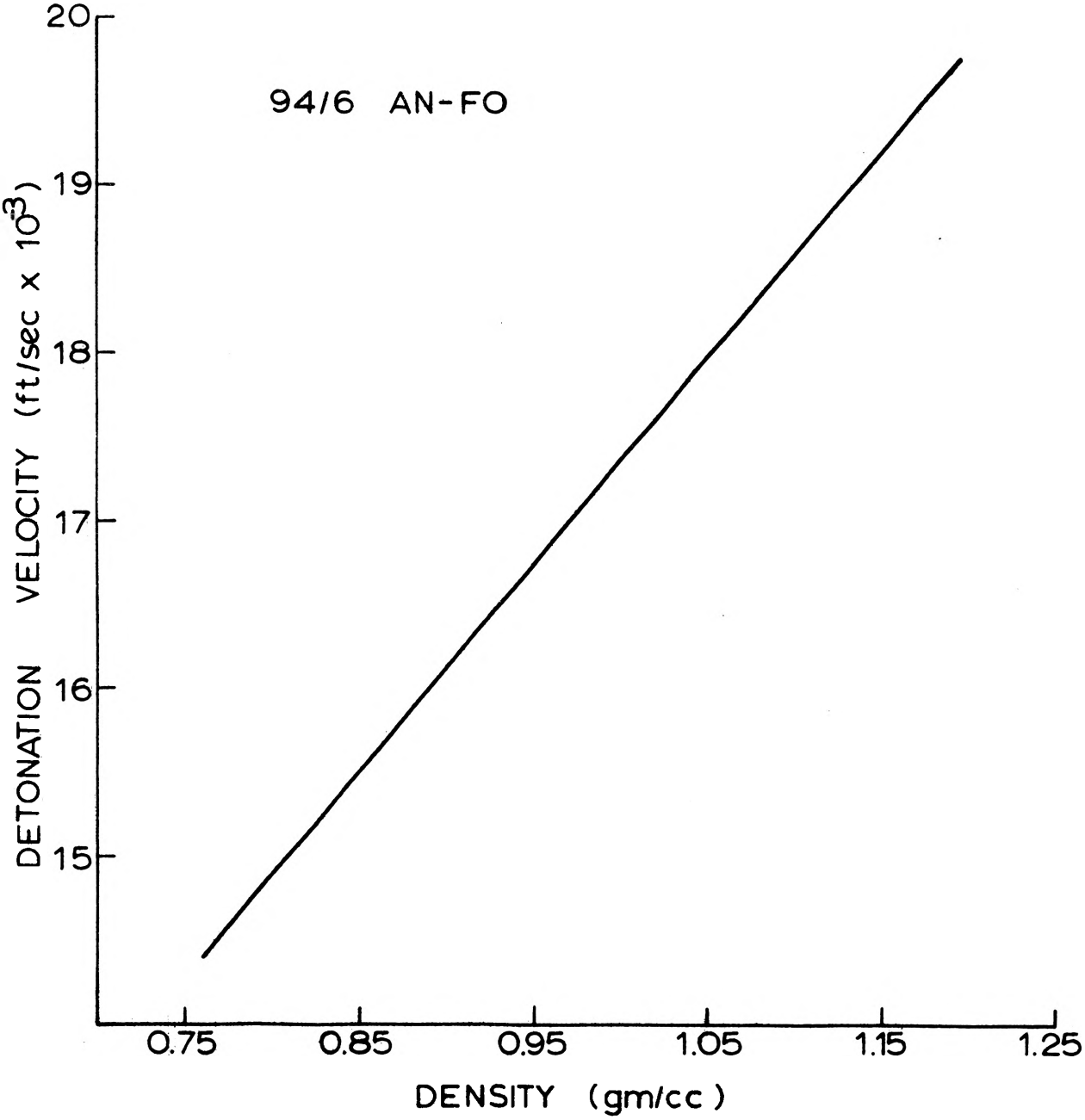
APPENDIX



VARIATION IN IDEAL DETONATION VELOCITY WITH DENSITY

FIGURE 13

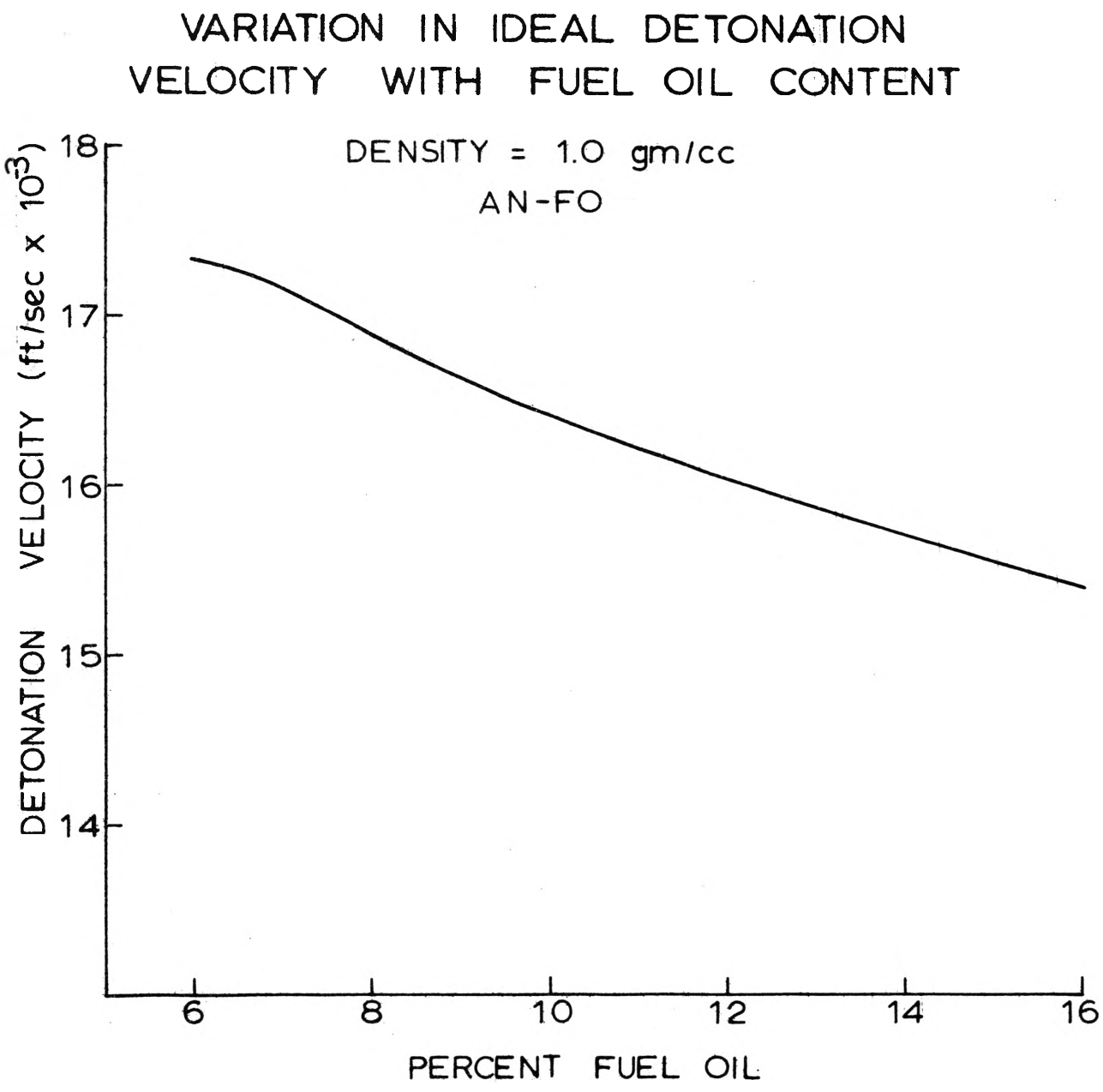

VARIATION IN IDEAL DETONATION
VELOCITY WITH FUEL OIL CONTENT
DENSITY = 1.0 gm/cc
AN-FO
DETONATION VELOCITY (ft/sec x 10^3)
18
17
16
15
14
6
8
10
12
14
16
PERCENT FUEL OIL

FIGURE 14

TABLE IV

DETONATION VELOCITY FIELD TEST DATA

Mesh Size (USSS)	Loading Density (gm/cc)	Average Dia. (microns)	Primer	Detonation Velocity* (ft/sec)
8/20	1.04	1520	(a)	9,020
"	1.04	"	(b)	9,260
"	1.06	"	(c)	9,260
12/20	1.01	1260	(d)	12,820
"	1.04	"	"	12,880
20/30	0.97	715	(e)	14,040
30/40	1.03	505	"	15,260
"	1.04	"	"	15,440
"	1.09	"	"	15,280
40/50	0.89	359	"	14,330
"	0.90	"	"	14,150
50/60	0.91	274	"	15,090
60/80	0.88	213	"	14,710
"	0.88	"	"	14,670
80/140	0.85	141	"	14,580
"	0.85	"	"	14,670
140/200	0.72	90	"	13,350

* 3 inch diameter iron pipe.

(a) Propellex #151

(b) 1200 grams composition C-4

(c) 1560 grams composition C-4

(d) 780 grams composition C-4

(e) 4-half sticks 60 percent ammonia dynamite

TABLE V

SENSITIVITY FIELD TEST DATA
(94/6 AN-FO, 3-inch dia. iron pipe)

Mesh Size (USSS)	Loading Density (gm/cc)	Detonation*		
		Complete	Partial	None
8/20	1.04	Propellex 151 1160 gm C-4 1560 gm C-4 1200 gm C-4	Propellex 151 Titan 150	40, 50, 50 21.5 gm PETN 4-½ sticks 60% Ammonia dynamite-(3 times)
12/20	1.00	780 gm C-4 (2 times)	50, 50	
20/30	1.00	50, 40, 40	30	
30/40	1.07	40, 30	30, 30, 25, 35	
40/50	1.01	10	10, 8	6
50/60	0.94	8	5	
60/80	0.86	4, 3, 2		2
80/140	0.83	2, 2, 1	1	1
140/200	0.71	1, 1		
-200	0.73	2		1

* Unless otherwise designated, numbers in these 3 columns refer to the number of blasting caps used.

Propellex 151 is a cast primer, 2 inches thick by 3 inches in diameter, manufactured by the Propellex Chemical Division of the Chromalloy Corporation, Edwardsville, Illinois.

Titan 150 is a cast primer of 150 grams weight, produced by the Hercules Powder Company, Wilmington, Delaware.

VITA

Robert B. Hopler, Jr. was born March 3, 1932, in Madison, New Jersey, the son of Robert B. and Margaret O. Hopler. He received his elementary and high school education in Madison.

In September 1950 he enrolled in the University of Missouri, School of Mines and Metallurgy, and graduated in May 1954 with a B.S. degree in Mining Engineering, Mining Geology option. At this time he also received a commission in the U.S. Army Reserve. In June 1954 he began employment as a mining engineer with the St. Joseph Lead Company, Bonne Terre, Mo. In October 1954 he entered the U.S. Army Chemical Corps and was assigned as a chemical materiel instructor on the Staff and Faculty of the Chemical Corps School, Fort McClellan, Alabama. He attained the rank of first lieutenant while on active duty.

He returned to the St. Joseph Lead Company in October 1956 and worked as a mine engineer on various underground projects. He ultimately was mine shift foreman over approximately 40 men. In the Army Reserve, he remained active during this period as company commander of an infantry heavy weapons company.

Besides professional experience with the St. Joseph Lead Company, he worked the summer of 1951 in an underground zinc mine in New Jersey, and the summer of 1952 at an Alaskan gold-dredging operation.

He was married to Helen M. Gaddy in December 1954.

In September 1959 he returned to the Missouri School of Mines for graduate study. He was granted an assistantship in the Department of Mining Engineering in February 1960. He is a member of Theta Tau, Sigma Gamma Epsilon, a junior member of the American Institute of Mining Engineers, and an associate member of Sigma Xi.